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A STUDY OF ION COMPOSITION AND CHEMISTRY IN A QUIET, MIDDAY, MIDLATITUDE F-REGION FROM 130 TO 306 KILOMETERS

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June 1969

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ABSTRACT

Altitude profiles of ion composition and concentration at midday from 130 to 360 kilometers were measured by a rocket-borne Bennett ion mass spectrometer aboard NASA 18.06 above Wallops Island, Virginia, on August 26, 1966. Adopting Jacchia's 1964 neutral atmosphere model and previously published measurements of the EUV spectrum, the ion distributions are employed to deduce the reaction rates for the primary thermospheric processes

$$N_2^+ + O \rightarrow NO^+ + N$$

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2$$

$$O^+ + N_2 \rightarrow NO^+ + N$$

$$O^+ + O_2 \rightarrow O_2^+ + O$$

$$N^+ + O_2 \rightarrow O_2^+ + N$$

under the assumption of photochemical equilibrium. This is accomplished by considering separately the particle balance for each ion species. Starting with the ion constituent least dependent on the others, a hierarchy is established that allows a systematic and almost unique determination of the rate coefficients, which we find to be comparatively low and within a factor of three of the values derived in laboratory experiments. This result is regarded as demonstrating general agreement, considering the range of uncertainties attributed to the laboratory rate coefficients and to the estimated photoionization and recombination rates.

CONTENTS

A STUDY OF ION COMPOSITION AND CHEMISTRY IN A QUIET, MIDDAY, MIDLATITUDE F-REGION FROM 130 TO 306 KILOMETERS

INTRODUCTION

Previous attempts to determine the ion chemistry from ion composition profiles have been made by Swider [1965], Bauer [1966], Brinton et al. [1969a], Holmes et al. [1964], and Johnson et al. [1967]. However, in a recent review paper Donahue [1968] pointed out the need for more measurements of ion composition. In this paper vertical profiles of F-region positive ion composition measured above Wallops Island, Virginia, on August 26, 1966, are presented and analyzed using correlative data obtained from other experiments conducted during the same time period or under similar conditions. To evaluate the processes which are responsible for the production and loss of ions in the F-region, it is necessary to measure or have knowledge of many other parameters including the spectrum of ionizing radiation, ionization crossections, neutral and charged particle concentrations and temperatures, recombination coefficients, and reaction rates. Coefficients of the primary chemical reactions responsible for the formation of the ionosphere are derived in this study, which is based on ion composition measurements, obtained from NASA 18.06 which was launched by a Nike-Tomahawk rocket at 1351 LT (1851 UT). The cylindrical pressurized package which contained experiments to measure thermal positive ion composition and concentration, neutral N_2 temperature and density, and electron temperature and density was one of three Thermosphere Probes in a series of six complimentary

soundings conducted during a 34 hour period. The additional experiments measured N_2 temperature and density, electron temperature and density, and neutral composition, and obtained information about the incoming solar EUV radiation. The launching of four of the sounding rockets occurred within one hour of an orbital pass of the Explorer 32 (Atmospheric Explorer-B) Satellite to enable a further comparison of measurements made by similar instruments in the nearly the same regime [Spencer et al., 1967]. A comparison of the ion spectrometer data has been discussed in another paper by Brinton et al. [1969b].

THE ION SPECTROMETER

Since the operation of the Bennett spectrometer was described previously in the literature [Taylor et al., 1963, 1965], only characteristics of the spectrometer and sensor which were unique to this flight will be discussed. A cylindrically shaped package enclosed the Bennett ion spectrometer ceramic sensor tube, electronic instrumentation, and earth telescope (a part of the optical aspect system) to form one end of the trisectional Thermosphere Probe. The sensor, a 7-5 cycle tube with an inter-grid spacing of three millimeters, was mounted co-axially in one end of the package and operated at a frequency of 5.4 MHz. The ion mass range was scanned from 12 to 36 amu every 0.15 seconds. Two sensitivities were achieved by switching the stopping voltage at the end of each sweep.

RESULTS

Ion Current Data

The tumble period of the experiment package was relatively long ($\approx$ 45 seconds) compared to the spectrometer sweep rate (0.15 seconds). The ion spectrometer orifice was oriented at angles of attack which varied from a few degrees to $\approx$ 180 degrees over large altitude ranges, producing a strong modulation of the ion currents. Ions detected were 14^+, 16^+, 28^+, 30^+, and 32^+, which were identified as N^+, O^+, N_2^+, NO^+, and O_2^+. Some 18^+ was observed which was identified as H_2O^+ created by charge exchange from the outgassing of H_2O from the experiment.

Ion Composition

A technique for normalizing the total ion current detected during each spectral sweep to a curve of total ion concentration (N_i) was used to correct for aspect and to derive the concentrations of the individual ion constituents. This curve was established by assuming $N_i = N_e$ and by normalizing (at F-maximum) the smoothed profile of electron concentration (N_e) measured by the NASA 18.06 electrostatic probe [Brace, personal communication] to a curve resulting from ground based ionosonde measurements from 130 to 240 kilometers. The electrostatic probe thus provided an extrapolation of the ionosonde profile from F-maximum to peak altitude. Before normalization to the total ion concentration curve, the individual ion current measurements were corrected for mass discrimination using factors determined from laboratory studies. After the normalization process the respective ascent and descent concentrations of each ion

(which were within a factor of two in agreement) were smoothed to produce the final profiles presented in Figure 1.

DISCUSSION

Photo-chemical reactions are primarily responsible for the ion distributions in the lower ionosphere (up to 250 km). Thus ion composition measurements constitute a valuable tool to deduce and test the rate coefficients that are involved in these reactions.

In the following analysis we adopted the EUV spectrum and the absorption and ionization cross sections published by Hinteregger et al. [1965]. Spectroscopic measurements of a few lines in the EUV range, made on a rocket flight only 40 minutes before the 18.06 flight [Hinteregger, personal communcation] showed an enhancement in some lines of the measurement of Hinteregger et al. [1965]; however other lines showed a decrease of the photon flux intensities. Since we could not find a justification to scale the earlier and more complete spectrum in either direction, we assumed it as representative of flux at the time of this measurement. During the 18.06 flight, a solar flare occurred, accompanied by an x-ray event that was recorded on the Solar Radiation Monitoring Satellite of the Naval Research Laboratory (NRL) [Lincoln, 1966]. Since in comparing these measurements with Hinteregger's XUV range we found that the x-ray enhancement during the flare increased with decreasing wave lengths, we normalized Hinteregger's spectrum below 200 Å to the NRL satellite measurements. For the ionization efficiency, it was assumed that one electron-ion pair was produced per 25

ev of photoelectron energy. Therefore, the efficiency factor was assumed to be

$$Eff = \frac{E_{ph}}{25}$$

where E_{ph} is the energy of a photon (in ev) for wave lengths smaller than 350 Å; above 350 Å the efficiency factor was assumed to be unity. Adopting Jacchia's model [1964] for the neutral composition with an exospheric temperature of 1050°K, based on the observed 10.7 cm flux, the ionization rates, including primary and secondary ionization were calculated and are shown for O^+, N_2^+, and O_2^+ in Figure 2.

N_2^+ Ions

Production of N_2^+ ions is by photoionization of N_2. The production rate is shown as a dotted line in Figure 2. N_2^+ ions are lost primarily by the reactions

$$N_2^+ + O \rightarrow NO^+ + N \qquad \left[k_{N_2^+ O}\right] \tag{1}$$

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2 \qquad \left[k_{N_2^+ O_2}\right] \tag{2}$$

[Ferguson, 1967], and by

$$N_2^+ + e \rightarrow N + N \qquad \left[k_{N_2^+ e}\right] \tag{3}$$

[Biondi, 1967]. The dissociative recombination coefficient is electron-temperature (T_e) dependent, with

$$k_{N_2^+e} = k_{N_2^+e_0}\left(\frac{300}{T_e}\right)^{0.4}$$

and where the constant

$$k_{N_2^+e_0} = 2.5 \times 10^{-7}\ \mathrm{cm^3\ sec^{-1}}$$

[Biondi, 1967]. For T_e we assume a linear altitude distribution of

$$T_e = T_{e_{130\,km}} + k\left(z - z_0\right) \qquad (4)$$

with

$$T_{e_{130\,km}} = 700\,^\circ\mathrm{K}$$

$$z_0 = 130\ \mathrm{km}$$

$$k = 7$$

which is consistent with rocket measurements [Brace et al., 1969]. Using the photoproduction rates of N_2^+ shown in Figure 2 and the measured concentrations of N_e, NO^+, and O_2^+, the N_2^+ continuity equation was solved using the reactions (1-3) and by varying $k_{N_2^+O}$ and $k_{N_2^+O_2}$ to provide an optimum fit of calculated to the observed N_2^+ profiles. The resulting values are

$$k_{N_2^+O} = 9.5 \times 10^{-11}\ \mathrm{cm^3\ sec^{-1}}$$

and

$$k_{N_2^+O_2} = 7.2 \times 10^{-11}\ \mathrm{cm^3\ sec^{-1}}\ .$$

These values are lower than those summarized by Ferguson [1967] by about a factor of two, which is approximately the uncertainty for the ionization cross sections [Hinteregger, personal communication].

NO$^+$ Ions

Production of NO$^+$ ions is by reaction (1) and by reactions

$$O^+ + N_2 \rightarrow NO^+ + N \qquad \left[k_{O^+N_2}\right] \tag{5}$$

$$N^+ + O_2 \rightarrow NO^+ + O \qquad \left[k_{N^+O_2}\right] \tag{6}$$

[Ferguson, 1967]. Loss of NO$^+$ is by dissociative recombination

$$NO^+ + e \rightarrow N + O \qquad \left[k_{NO^+e}\right] \tag{7}$$

with an electron-temperature coefficient of

$$k_{NO^+e} = k_{NO^+e_0} \left(\frac{300}{T_e}\right)^{1.2} \tag{8}$$

where the constant

$$k_{NO^+e_0} = 5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$$

[Biondi, 1967].

Since the O_2 concentration [Jacchia, 1964] is at least a factor of five lower than the N_2 concentration and the measured N^+ concentration is nearly two orders of magnitude lower than the measured O^+ concentration over the entire

altitude range (see Figure 1), we can neglect reaction (6). With the knowledge of the previously observed coefficient, $k_{N_2^+O}$, we then deduce from our measurements and reactions (1) and (5) the coefficient for reaction (5) to be

$$k_{O^+N_2} = 9.5 \times 10^{-13}\ \mathrm{cm^3\ sec^{-1}}\ .$$

Laboratory measurements of this reaction rate coefficient gave an upper limit of $6.7 \times 10^{-12}\ \mathrm{cm^3\ sec^{-1}}$ [Talrose et al., 1962]. Measurements by Fehsenfeld et al. [1965b] resulted in a value of $3.0 \times 10^{-12}\ \mathrm{cm^3\ sec^{-1}}$. Schmeltkopf et al. [1966] reported that this reaction rate may sharply depend on the vibrational temperature of N_2, and this may explain some of the higher values for $k_{O^+N_2}$ that were reported in the literature. Thus we feel justified to consider our value as reasonable, again considering the uncertainty in the EUV measurements.

O^+ Ions

The O^+ ions are produced by photoionization and by the charge exchange reaction

$$N_2^+ + O \rightarrow O^+ + N_2 \qquad \left[k_{N_2^+O}\right] \qquad (9)$$

Ferguson et al. [1965] estimate the reaction coefficient for (9) to be smaller than $10^{-11}\ \mathrm{cm^3\ sec^{-1}}$. Considering the N_2^+ density when compared to the O^+ density (Figure 1) that is involved in the subsequent loss reaction, we may neglect (9).

The O^+ ions are removed by reaction (5) and by

$$O^+ + O_2 \rightarrow O_2^+ + O \qquad \left[k_{O^+O_2}\right] \qquad (10)$$

[Ferguson, 1967].

Employing the production rate for O^+ as shown in the dashed line in Figure 2 and the previously derived rate coefficient, $k_{O^+N_2}$, we find that a coefficient for reaction (10) of

$$k_{O^+O_2} = 3.75 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$$

is in best agreement with the O^+ measurements of the 18.06 flight. For this rate coefficient the values that occur in the literature vary between 1.8×10^{-12} [Langstroth and Hasted, 1962] to 4×10^{-11} cm^3 sec^{-1} [Fehsenfeld et al., 1965a].

O_2^+ Ions

The O_2^+ ions are produced by photoionization (the rate of which is shown in Figure 2 as a solid line), by reactions (2) and (10), and according to Fehsenfeld et al. [1965c]

$$N^+ + O_2 \rightarrow O_2^+ + N \qquad \left[k_{N^+O_2}\right]. \qquad (11)$$

Removal of O_2^+ is by dissociative recombination

$$O_2^+ + e \rightarrow O_2 \qquad \left[k_{O_2^+e}\right] \qquad (12)$$

with

$$k_{O_2^+ e} = k_{O_2^+ e_0} \left(\frac{300}{T_e}\right)^{0.5}$$

where

$$k_{O_2^+ e_0} = 2.2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$$

[Biondi, 1967]. Since the reaction rates $k_{O^+O_2}$ and $k_{N_2^+O_2}$ were derived earlier, under the assumption of photo-chemical equilibrium the coefficient for $k_{N^+O_2}$ can be estimated. Our analysis has shown that its value should not be larger than

$$k_{N^+O_2} = 3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} ,$$

which is slightly lower than the laboratory values summarized by Ferguson [1967] which vary from 4.5×10^{-10} to 5.0×10^{-5} cm^3 sec^{-1}.

The production mechanisms (2), (10) and (11) and the ionization rate for O_2^+ increase at lower altitudes, while the recombination rate (which is proportional to N_e) tends to decrease. Consequently one should expect an increase of O_2^+ in the altitude range down to 130 km. In fact, we see from the 18.06 experiment a leveling off in the O_2^+ concentration below 160 km.

Several factors could account for this discrepancy. The temperature-dependent recombination coefficient could possibly increase much faster, which might be due to a faster decrease in the electron temperature at lower altitudes. Although this certainly may contribute to change the O_2^+ distribution in the desired way, the relatively weak temperature dependence of the recombination coefficient makes it unlikely to account quantitively for this effect. Another possibility is that the photoionization rate for O_2^+ is actually lower than we assumed. For this case the total production rate would be more significantly decreased at lower altitudes where the other production mechanisms involving O^+, N^+, and N_2^+ (which decrease with altitude) become less effective. Danilov [1969], having similar difficulties in explaining O_2^+ and NO^+ concentrations at lower altitudes, suggests that the reaction

$$O_2^+ + N \rightarrow NO^+ + O \tag{13}$$

may be of significance if one invokes an N concentration of 10^8 cm^{-3} at 110 km and a reaction rate for (13) of 2×10^{-10} cm^3 sec^{-1}.

In order to check the consistancy of our results, the coupled continuity equations for O^+, N_2^+, NO^+, and O_2^+ and the previously discussed ion chemistry reactions were solved for the altitude distributions of these ion species, assuming photo-chemical equilibrium and using the previously derived reaction rate coefficients. The measured ion profiles diverged from the calculated distributions above 230 km, indicating that diffusion processes are important above this altitude. A computation for N^+ was not performed, because it involves the He^+

concentration, which was not measured in this experiment. However, the measured N^+ distribution was adopted as an input to allow consideration of the reactions involving this species.

The agreement between measured and calculated ion distributions below 230 km, shown in Figure 3, is rather good. The only significant exception is O_2^+ at lower altitudes, which as already mentioned, might indicate that the adopted photoionization cross sections for O_2^+ are too high. The discrepancy in NO^+ at lower altitudes may be due to our overestimation of O_2^+ which leads to higher electron densities; consequently the recombination rate is increased for NO^+, from which lower NO^+ values follow.

One must keep in mind that the variability of the neutral composition, plasma temperatures, and the UV spectrum of the sun induce variations in the ion composition. For example, Johnson [1967] shows a crossover in the O_2^+ and NO^+ distributions at about 140 km, which is consistent with the theoretical model we have shown. However, it differs from our measured profiles which show that the distributions of O_2^+ and NO^+ are parallel. Brinton et al. [1969a] show a crossover at about 260 km, but the tendancy for the two ions to be nearly equal below this height makes the assignment of the exact altitude of this crossover very difficult. Danilov et al. [1969] show O_2^+ and NO^+ almost equal from 130 to 155 km eak altitude), in near agreement with Brinton et al. [1969a].

This clearly indicates that ionospheric processes can only be evaluated when simultaneous measurements are made of the many physical parameters

involved. These measurements are planned for future multi-experiment low altitude satellites.

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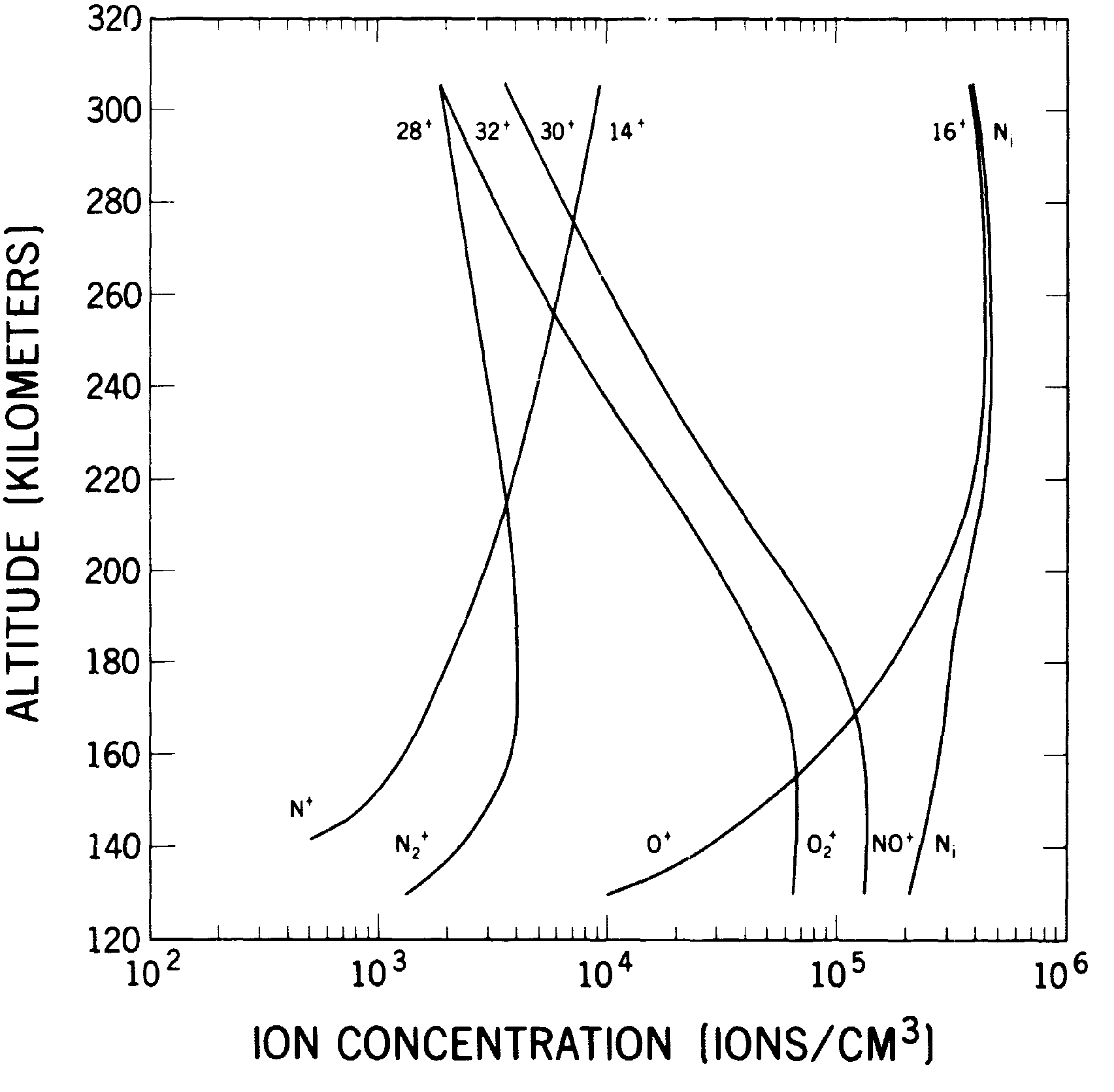

Figure 1. Altitude profiles of measured ion concentrations, an average of the ascent and descent data derived by normalizing the ion currents to the total ion concentration, N_i, which results from ground based ionosonde measurements and electrostatic probe data.

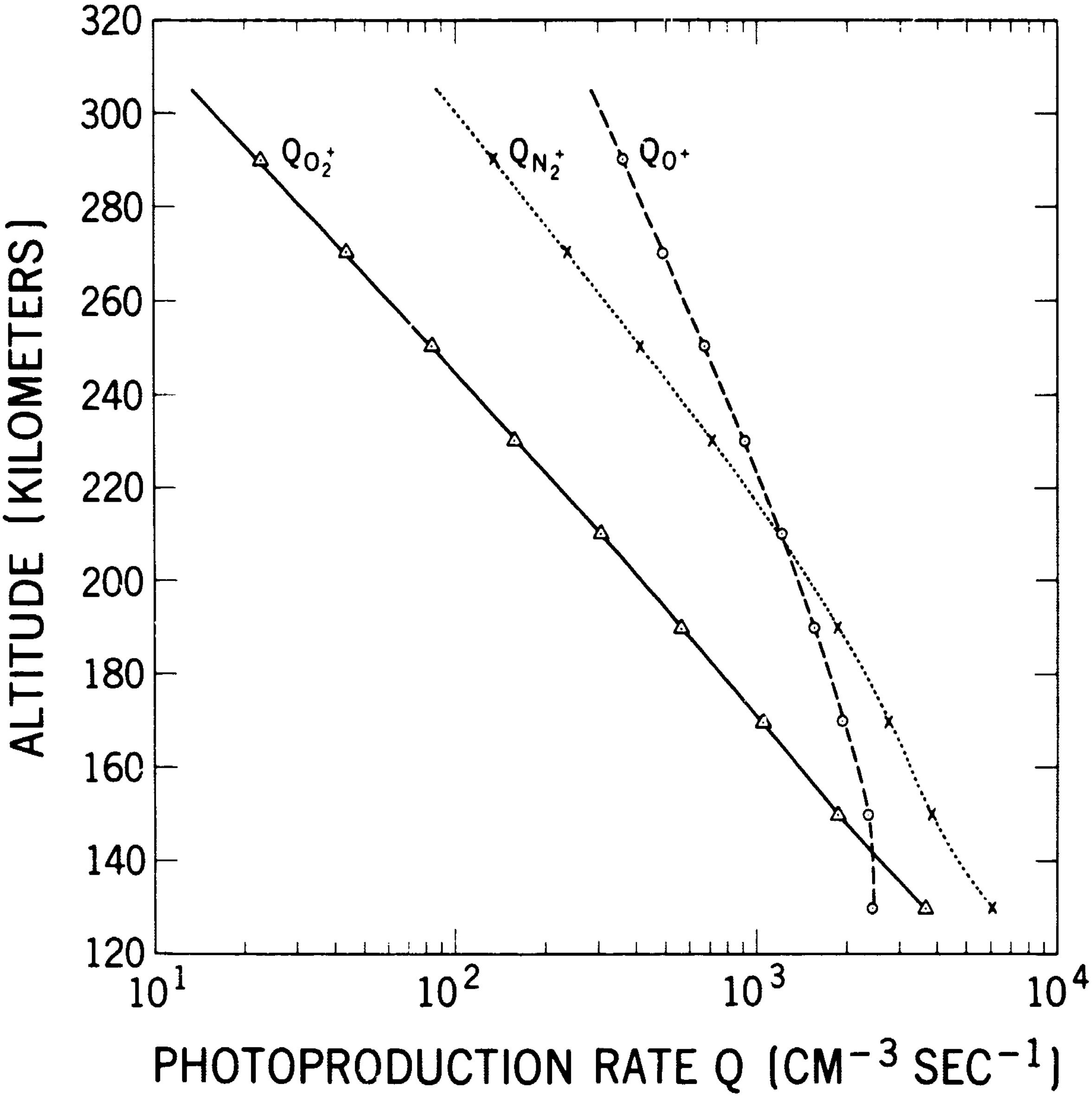

Figure 2. Calculated photoproduction rates for O_2^+, N_2^+, and O^+ based on EUV measurements by Hinteregger et al. [1965] and the Solar Radiation Monitoring Satellite of NRL.

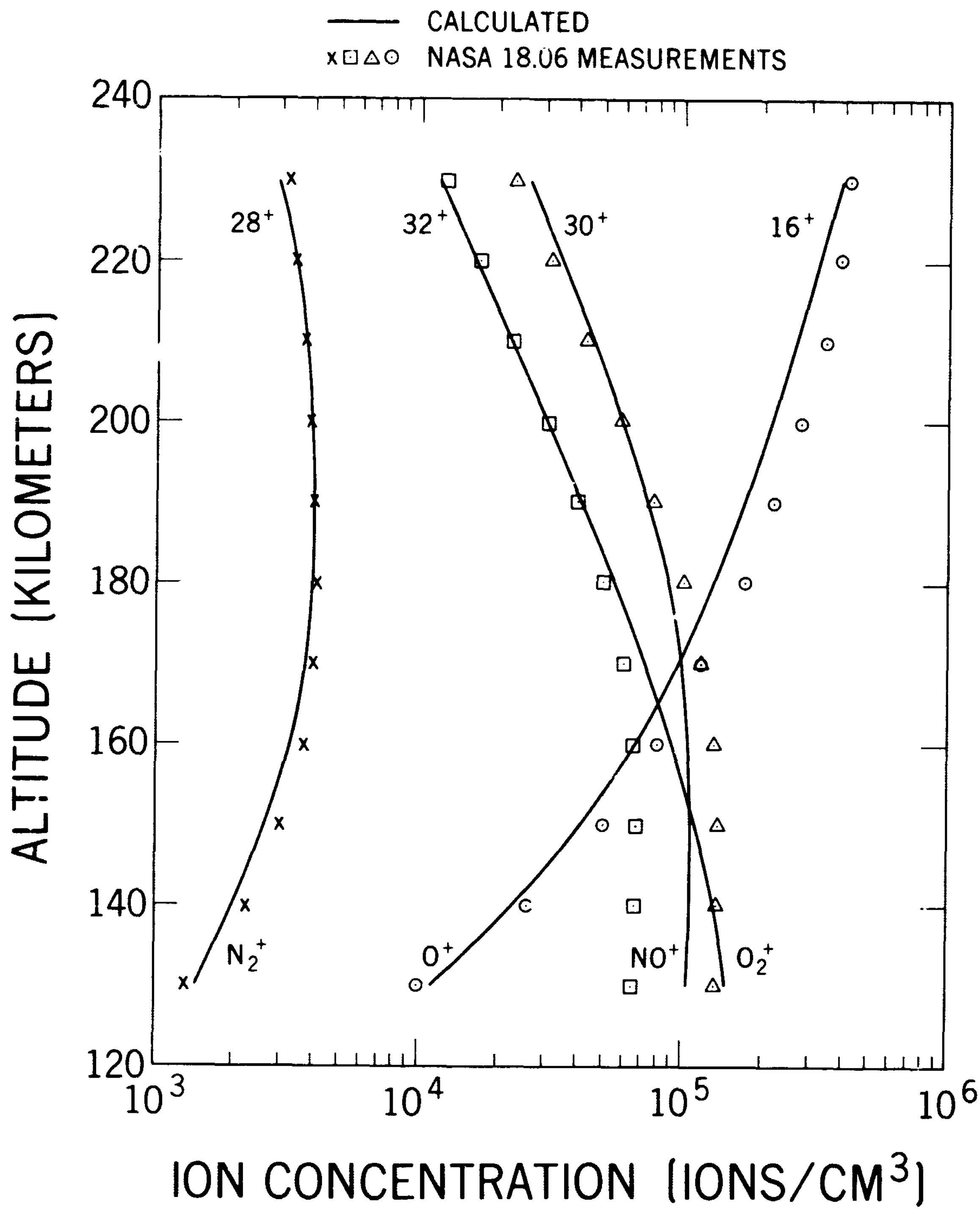

Figure 3. Comparison of altitude profiles of ion concentrations calculated assuming photochemical equilibrium and derived reaction rates with the ion concentrations measured by the ion spectrometer on NASA 18.06.